ARO 19141.3-CH

2

SPECTROSCOPIC INVESTIGATIONS OF ORGANIC MOLECULES ON GRAPHITE SURFACES

FINAL REPORT

AD-A165 431

Richard H. Clarke
Department of Chemistry
Boston University

February 25, 1986

U.S. Army Research Office

DAAG 29-82-K-0124

Submitted by Boston University

Approved for Public Release;
Distribution Unlimited.

255

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MASTER COPY - FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER ARO 19141.3-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Spectroscopic Investigations of Organic Molecules on Graphite Surfaces		5. TYPE OF REPORT & PERIOD COVERED 1 Jul 82 - 31 Dec 85 FINAL REPORT
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Richard H. Clarke		8. CONTRACT OR GRANT NUMBER(s) DAAG29-82-K-0124
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Boston University		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE February 26, 1986
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

graphite, surface spectroscopy, raman, ODMR,

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The final report describes work on the spectroscopy of organic aromatic molecules boubd to the surface of graphite. The experiments performed include' raman, ODMR, surface emission and reflectancespectroscopy.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ARO FINAL REPORT

Introduction:

The research program conducted over the past three years under ARO sponsorship focused on the spectroscopic investigation of polycyclic aromatic molecules adsorbed onto the surface of graphite. The overall aim of the investigation was to characterize the structural features of the adsorbed complex and to identify the nature of the interactions which stabilize them. Our approach was to examine a series of prototypical aromatic molecules bound to highly oriented pyrolytic graphite by optical, magnetic resonance, and raman spectroscopy.

Summary of Important Research Results:

Results in several areas of significance were obtained in the course of the research program. In summary, these were:

1. observance of optical and ODMR spectra of photoexcited quinoline and quinoxaline on graphite
2. observance of resonance raman scattering from chlorophyll on graphite
3. observance of ODMR from chlorophyll on graphite
4. determination of the chlorophyll geometry on the graphite surface
5. demonstration of the feasibility of raman-detected ODMR on surfaces.

The ability to prepare and detect at the monolayer level the spectroscopic properties of organic molecules on a surface, one of the principal goals of the program, is clearly demonstrated in each of these research results.

In detail, we have shown for the first time that photoexcited triplet state zero-field magnetic resonance transition may be observed using the raman peak intensities to monitor the microwave induced population changes effected in the triplet state. This approach allows a complex molecular system, such as can occur on a metal surface in which molecules may be found at a variety of binding sites or in aggregated domains distributed on the surface, to be sorted out on the basis of its raman spectrum; then only the molecules of interest identified by their characteristic raman bands are monitored for their triplet state features. We have employed this approach to investigate the chlorophyll-graphite system and have been able to separate monomeric and aggregate features of the chlorophylls bound to the graphite surface.

Of particular interest to our group has been the use of observed raman and ODMR spectra of the chlorophyll molecule on graphite to determine the orientation of the chlorin ring system relative to the binding surface. Our simulation of the ODMR results indicated that the chlorin ring sits on the surface at about a 65 degree angle. This result was initially surprising in that the expected orientation was parallel to the surface, if the molecule was stabilized by pi overlap between the chlorin ring electrons and the pi-type band structure of the graphite. These results indicated clearly that the interactions stabilizing the bound molecules on a metal surface, even in the prototype graphite system, were not simple.

In addition to the chlorophyll ODMR experiments we sought to confirm the orientational features on graphite by performing polarized raman experiments with the laser field polarization fixed parallel and perpendicular to the graphite surface. The variation of polarization ratios over the raman bands over the totally symmetric modes made the determination of orientation angle less specific than in the ODMR case, but the two results - from quit different experimental approaches - were consistent.

In contrast to the chlorophyll case, our experiments with quinoline and quinoxaline indicated that a preferred orientation on the graphite surface is not maintained for all molecular systems. In fact, a series of careful experiments to deposit the molecules under differing conditions (vapor deposition, evaporation, spinnig droplets on the surface) indicated that sample preparation conditions may be the dominant influence on the surface spectroscopic properties observed from the smaller adsorbed molecules.

Publications resulting from the present research:

R. H. Clarke and E. B. Hanlon
ODMR and Resonance Raman Spectroscopy of Chlorophyll B on Graphite
J. Chem. Phys., 82, 5275 (1985)

R. H. Clarke, D. J. Graham, and E. B. Hanlon
Triplet State ODMR of Molecules Adsorbed to the Surfaces of Bulk Metals
Photochemistry and Photobiology (A. Zewail, ed.), 2, 1011 (1983)

R. H. Clarke, D. J. Graham, E. B. Hanlon, and P. Mitra
Resonance Raman Detected Triplet State Magnetic Resonance
J. Chem. Phys., 79, 1549 (1983).

Scientific Personnel Engaged in the Research:

Prof. Richard Clarke, Principal Investigator
Dr. Daniel Graham, Postdoctoral Research Associate
Dr. Robert Gillies, Postdoctoral Research Associate
Eugene Hanlon, Graduate Research Assistant, Ph.D. received, 1985
Sreekham Nair, Graduate Research Assistant, M.S. received, 1984